

# Production of Bio-oil from Alfalfa Stems by Fluidized-Bed Fast Pyrolysis<sup>†</sup>

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This study focused on the production of bio-oil from alfalfa stem material. Two alfalfa maturity stages, harvested at the early bud and full flower stages of development, were examined to evaluate the impact of variation in cell wall polysaccharide and lignin content on pyrolysis oil yields, production efficiency, and bio-oil and char quality, in terms of their use as combustion fuel and for chemicals. Findings included a lower-than-average yield of bio-oil and a higher-than-average yield of charcoal from alfalfa stems, compared to previous results for other biomass feedstocks. The bio-oil showed a decrease in oxygen content from the alfalfa stems, leading to a higher-than-average energy content in the bio-oil. Bio-oil yields were slightly higher for the more-mature alfalfa, which had higher levels of cell wall cellulose and lignin. Overall, when all the pyrolysis products were considered, energy recovery was better for the more-mature alfalfa stems.

## 1. Introduction

Alfalfa (*Medicago sativa* L.) is the third most widely grown crop in the United States, with an annual average acreage of more than 9.3 million ha.<sup>1</sup> In 2006, the U.S. alfalfa production for dry hay was more than 65 million metric tons, with a total direct value of more than \$7.5 billion.<sup>2</sup> Alfalfa is a perennial legume that is primarily used as high-quality forage for livestock feed, because it contains a high amount of crude protein, provides dietary fiber needed to maintain rumen health, and is an excellent source of vitamins and minerals. Alfalfa also improves soil health, through its symbiotic relationship with the soil bacterium *Sinorhizobium meliloti*, resulting in biological N<sub>2</sub> fixation. On average, alfalfa fixes 150 kg of nitrogen/ha, on an annual basis.<sup>3</sup> The greatest portion of the fixed nitrogen is removed by forage harvest, but fixed nitrogen also is added to the soil for use by subsequent crops. Because of its high biomass yield and perennial nature, alfalfa is an excellent potential source of biomass for cellulosic ethanol and other biofuels applications.<sup>4</sup> In an alfalfa biomass energy production system, the forage could be fractionated into stems and leaves. The stems could be processed to generate electricity or biofuels, and the leaves could be sold as a supplemental protein feed for livestock.<sup>5</sup> One of the advantages of using alfalfa to produce biomass energy, compared to other crops, is the secondary income stream from selling the leaves as a higher-value animal feed.

Lamb et al.<sup>6</sup> proposed a biomass-management system that was based on less-dense alfalfa stands harvested at more-mature stages of development than that done currently for livestock feed (late flower or early pod rather than early bud stage). In preliminary trials, the yield of total biomass increased by 30%, with all of the increase being due to more stem production and no change in leaf yield.<sup>6,7</sup> The delayed harvest of alfalfa in the biomass-management system increased the total cell wall concentration of the biomass by 6%, with glucans, xylans, and lignin accounting for most of the increase. Composition of the

cell wall material shifted toward more lignin (6%) and xylan (4%), and less pectin, because of a delayed harvest, but the glucan content of the cell wall did not change.<sup>8</sup>

The use of alfalfa stems for the production of ethanol via the biochemical conversion process has been studied by Dien et al.<sup>9</sup> They applied a dilute acid pretreatment to two stem samples of different maturity and found that the efficiency of glucose recovery and enzymatic saccharification of the stems correlated negatively with lignin content; this was similar to the negative impact of lignification on digestibility of the forage by ruminants. The biofuel potential of alfalfa stems was evaluated by Gray and Kaan.<sup>10</sup> They showed the stems to have favorable combustion characteristics, such as low ash and volatile contents, compared to some coals, except for its low energy content as a combustion fuel. Little information exists on other thermochemical conversion technologies such as alfalfa stem gasification or its pyrolysis. To our knowledge, production of bio-oil by fast pyrolysis as an alternative biofuel conversion process in alfalfa has not been studied, although analytical pyrolysis for characterization of lignin structure was performed by Ralph and Hatfield.<sup>11</sup>

The bio-oil production process is simple, not energy-intensive, and it has potential to produce energy-dense liquids and charcoal for soil augmentation, all of which make it amenable to farm-based distributed-energy systems. The current study focused on the production of bio-oil from two alfalfa stem sources of different maturity. Of interest was the effect of differences in traits such as cell wall carbohydrate and lignin content associated with alfalfa maturation on pyrolysis oil yields, production efficiency, and bio-oil and char quality, in terms of their use as a combustion fuel and as chemical feedstock.

## 2. Materials and Methods

**2.1. Plant Material.** Alfalfa biomass was collected from breeding nurseries located at Rosemount and Becker, MN in the summer of 2003. The source alfalfa populations for these nurseries were created by intercrossing commercial varieties. The nurseries had been planted in 2001; therefore, all plants were mature individuals when sampled. Plants were harvested at Becker on August 9 at the early bud stage of development

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<sup>†</sup> The mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

when stem shoots had flower buds, but no open flowers were present. Additional plants were harvested from the nurseries at Rosemount on August 19 at the full flower stage of development, when open flowers were found on every stem shoot. A single bulk sample was created for each harvest by combining all plants collected on that harvest date. Following harvest, the alfalfa biomass was air-dried in a forced-air oven at 60 °C and subsequently hand-separated into leaf (including floral components) and stem fractions. The stems were ground through a 2-mm screen in a Wiley mill.

For use as pyrolysis feedstock in the current study, each of the maturity stage bulk samples were subdivided into three replicate batches for individual analysis. In this report, the early bud alfalfa will be referred to as samples bud 1, bud 2, and bud 3, and the full flower samples are designated as flower 1, flower 2, and flower 3.

**2.2. Feedstock Compositional Analysis.** A complete compositional analysis was performed on the alfalfa samples that were used as feedstock for bio-oil production. These analyses included chemical composition, as well as elemental and proximate analyses. Proximate and ultimate (elemental) analyses were conducted on one replicate sample of each alfalfa maturity stage (samples bud 3 and flower 3), whereas the chemical composition analyses were conducted on all six feedstock samples. Proximate and ultimate analyses and higher heating value (HHV) determination were performed by Galbraith Laboratories, Inc. (Knoxville, TN), using ASTM methods D5291 and D240, respectively. Chemical composition included analysis of carbohydrate fractions as well as lignin using methods described by Dien et al.<sup>9</sup> Carbohydrate fractions included soluble sugars (glucose, fructose, and sucrose), starch, and cell wall polysaccharides (cellulose, hemicellulose, and pectin). The Uppsala Dietary Fiber Method was used to determine the neutral sugar and uronic acid residues of the cell wall polysaccharides, plus Klason lignin.<sup>12</sup> Cellulose was estimated as the cell wall glucose content, hemicellulose as the sum of xylose, mannose, and fucose residues, and pectin as the sum of uronic acids, arabinose, galactose, and rhamnose residues.<sup>13</sup> These analyses were performed in duplicate for each of the six alfalfa stem feedstock samples. The ash content and percent dry matter were also determined.

**2.3. Fluidized-Bed Fast Pyrolysis.** Pyrolysis was conducted in a bubbling fluidized bed of quartz sand at temperatures in the 400–550 °C range. The apparatus (Figure 1) is comprised of a 7.62-cm (3-in.)-diameter fluidized reactor section, two cyclones in series for gas cleanup, and a series of four condensing canisters that are cooled by a dry ice/water bath, followed by an electrostatic precipitator, which collects the largest fraction of the pyrolysis oil produced. The functions of each of the components described have been detailed by Boateng et al.<sup>14</sup> Temperature and pressure measurements were conducted using thermocouples and pressure transducers and logged using a Labview data acquisition and control system (National Instruments, Austin, TX). Mass balance was performed via gravimetric analysis of the feedstock used during the run and the bio-oil and charcoal products. The uncondensed gas composition was analyzed by gas chromatography (GC) (Agilent MicroGC 3001A). Gas quantity was determined by the difference between the fluidizing gas measured by a mass flow meter (Alicat Scientific, Tucson, AZ) and the effluent gas measured with a bulk gas flow meter (Metris). Energy flow in and out of the reactor was determined by the enthalpy and energy balances of the streams, using the mass flow rates, temperatures, and measured energy content of the bio-oil and char.

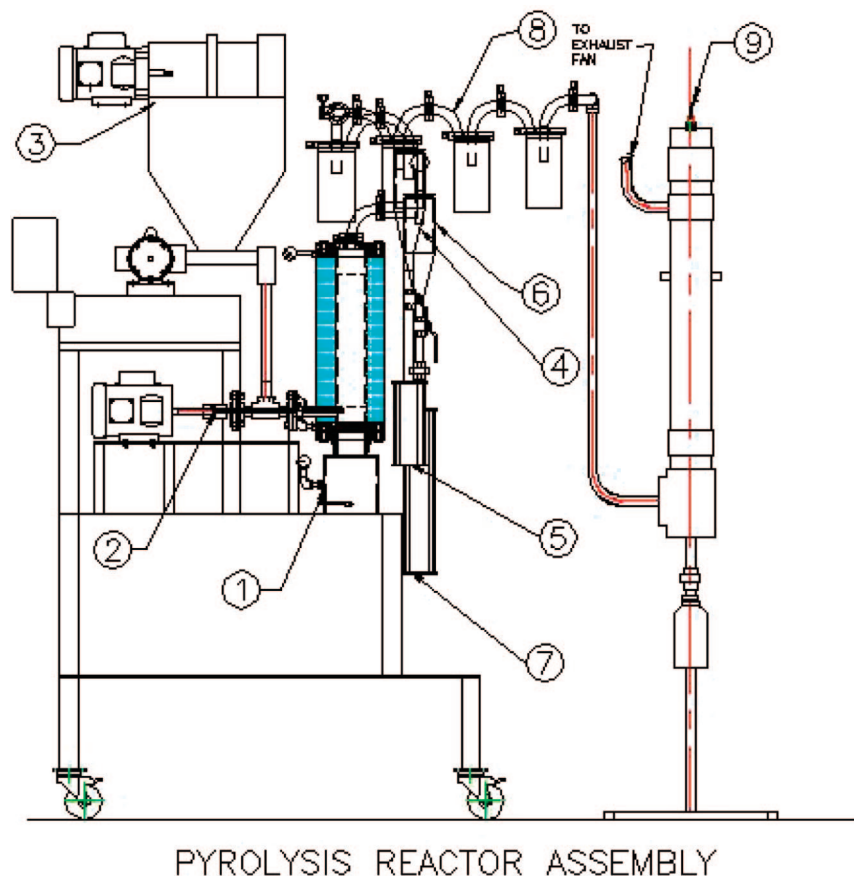
**2.4. Product Analysis.** The pyrolysis oil was analyzed for elemental carbon hydrogen nitrogen oxygen (CHNO) composition by ultimate analysis, liquid fuel characteristics, and chemical composition (including water, sugars, acids, and pertinent compounds). The char was analyzed for its fuel characteristics and composition, as well as its ash constituents and surface areas. The ultimate and fuel analyses were performed at Intertek Caleb Brett (Essington, PA) and at Galbraith Laboratories, Inc. (Knoxville, TN), using standard ASTM methods (D5291, D240, D4052). These analyses were conducted on two alfalfa stem feedstock samples of each alfalfa maturity stage (samples bud 1, bud 2, flower 1, and flower 2).

High-performance liquid chromatography (HPLC) analysis of the water-soluble fraction of bio-oil composition for concentrations of levoglucosan, acetic acid, acetol, and glyoxal was performed on a Waters Breeze HPLC system. Identification was done by comparison of retention times with authentic samples. A refractive index detector, set at 30 °C was used. The mobile phase was 0.007 N H<sub>3</sub>PO<sub>4</sub>. The column used was an Aminex HPX-87H, 300 mm × 7.8 mm column (Bio-Rad, Inc.), which was heated to 30 °C. The pump was programmed at a flow rate of 0.6 mL/min, and *n*-propanol was used as the internal standard for quantification.<sup>15</sup>

### 3. Results

**3.1. Biomass Composition.** The ultimate analysis of the alfalfa stem feedstock presented in Table 1 indicates only slight differences between samples harvested at the early bud and full flower stages of plant maturity. Notable differences were observed with the ash content and gross heating value but, on the dry-ash-free basis, the elemental composition of the two alfalfa stem maturity stages was similar. Concentration of total cell wall material in the alfalfa stems was greater at the full flower stage than at the early bud stage of maturity (see Table 2). Increased cellulose and Klason lignin concentrations accounted for the increase in cell wall material; however, the increases associated with maturation were relatively small. In contrast, concentrations of hemicellulose, pectin, and soluble sugars plus starch were quite similar for the two maturity stages. Free glucose and sucrose accounted for most of the soluble sugars plus starch fraction (data not shown). Although alfalfa stems do accumulate more total cell wall material, lignin, cellulose, and hemicellulose during their maturation because of proliferation of xylem tissues, this process is quite rapid and quickly reaches a relatively stable concentration of most of these components.<sup>16</sup> Even alfalfa germplasm selected for larger stems differ only marginally from fine-stem alfalfa at similar maturity stages.<sup>17</sup> Given this general lack of differences in alfalfa stem composition due to maturity stage at harvest, any difference in pyrolysis oil production and composition would be expected to be influenced by the difference in cellulose and lignin content, because these were the only components that differed between the two maturity stages.

**3.2. Product Yields and Energy Distribution.** Generally, the production of bio-oil from alfalfa stems presented several challenges. Critical observations include difficulty in maintaining the reactor temperature at the onset of feeding the reactor. There was an initial temperature rise at the onset of pyrolysis, although no inward air leakage was detected by GC. There was also a time delay in liquid flow, because of the highly viscous flow in the electrostatic precipitator (ESP). To ensure adequate flow, ESP temperatures were kept relatively high, which has an adverse effect on bio-oil production, because of the reduced quench rate. Table 3 presents the process operation under which



LIST OF MATERIALS		
ITEM	QTY	DESCRIPTION
1	1	REACTOR
2	1	BIOMASS FEED INJECTOR
3	1	GRAVIMETRIC FEEDER
4	1	PRIMARY CYCLONE
5	1	PRIMARY CHAR RECEPTACLE
6	1	SECONDARY CYCLONE
7	1	SECONDARY CHAR RECEPTACLE
8	1	CONDENSER
9	1	ELECTRODE ASSEMBLY

**Figure 1.** Schematic diagram of the pyrolysis reactor.

bio-oil production was conducted. While the feed rate during reactor operation varied among alfalfa stem feedstock samples, the reactor temperature range was small. Also, the biomass heat rates and the pyrolysis gas quench rates were approximately the same, which indicated similar bio-oil production conditions for the alfalfa stem feedstock samples. The average yields of pyrolysis products from the three samples within each alfalfa maturity stage are presented in Figure 2.

The average pyrolysis liquid yield from the early bud feedstock was 45%, compared to a value of 53% from the alfalfa stems harvested at the full flower stage. Charcoal production was high, with an average of 38.5% for early bud and 34% for full flower feedstock. The noncondensable gas from the early bud feedstock was 16.3%, compared to 12.8% for full flower alfalfa stems. The error in mass balance estimation was attributed to bio-oil that was trapped in the system and could not be physically recovered. These values accounted for 24%

and 21% of the bio-oil yield for the early bud and full flower maturity stages, respectively. The large nonrecovery of bio-oil was due to short experimental run durations, at a relatively small production capacity, exacerbated by the viscous nature of the bio-oil produced from alfalfa stems.

The energy balance estimates based on the input and output energy stream content showed very little variation. Of the average 6.9 kW of energy input into the reactor, including the early bud feedstock, 5.8 kW was output, a variation of 8%. For the runs with full flower alfalfa stems, the input and output energy streams were 7 kW and 6.5 kW, respectively, with an average variation of 4%. The output energy included the energy content of the pyrolysis products and the energy losses through the shell and the exhaust stream. The total reactor heat loss was estimated a priori. The energy in the product streams constitutes the useful energy recovered from the heat input and contained in the bio-oil, charcoal, and noncondensable gas. The amount



**Table 1. Original Alfalfa Stem Feedstock**

		Composition (wt %)		
		as received	dry basis	dry-ash-free (DAF) basis
Biomass at Early Bud (Bud 3)				
Proximate Analysis				
moisture		5.23		
ash		8.28	8.74	
volatile matter		69.55	73.39	80.41
fixed carbon		16.94	17.87	19.59
total		100.00	100.00	100.00
heating value				
[cal/g] <sup>a</sup>		4412	4655	5101
[kJ/kg]		18460	19478	21343
Ultimate Analysis				
moisture	18	4.97		
ash		7.87	8.28	
H	1	5.45	5.73	6.25
C	12	39.89	41.98	45.77
N	14	2.27	2.39	2.61
S	32	0.20	0.21	0.23
Cl	35	0.53	0.56	0.61
O	16	38.82	40.85	44.54
total		100.00	100.00	100.00
Biomass at Full Flower (Flower 3)				
Proximate Analysis				
moisture		5.57		
ash		5.51	5.83	
volatile matter		71.10	75.29	79.95
fixed carbon		17.83	18.88	20.05
total		100.01	100.00	100.00
heating value				
[cal/g] <sup>a</sup>		4480	4744	5037
[kJ/kg]		18740	19845	21074
Ultimate Analysis				
moisture	18	5.28		
ash		5.22	5.51	
H	1	5.53	5.84	6.18
C	12	41.12	43.41	45.94
N	14	1.43	1.51	1.60
S	32	0.08	0.08	0.09
Cl	35	0.37	0.39	0.41
O	16	40.98	43.26	45.78
Total		100.00	100.00	100.00

<sup>a</sup> Data taken from ref 24.**Table 2. Cell Wall, Carbohydrate, and Lignin Concentrations of Alfalfa Stem Feedstocks Harvested at Early Bud and Full Flower Stages of Development<sup>a</sup>**

trait	Concentration [g/kg DM]	
	early bud	full flower
cell wall	708	750
Klason lignin	141	169
cellulose	265	285
hemicellulose	122	123
pectin	134	130
soluble sugars plus starch	46	43

<sup>a</sup> Three replicate samples of each maturity stage were analyzed.

of energy input that is recovered in these products constitutes the energy efficiency (Figure 3). Although approximately 31%–42% of the recovered energy was in the bio-oil, energy recovered in the bio-oil and char combined was in the 64%–73% range and, when all the product streams are combined, the fraction recovered increased marginally, to 65%–74%.

**3.3. Alfalfa Stem Bio-oil Composition.** The bio-oil chemical composition quantified included water, water-soluble, and water-insoluble fractions. Reaction water produced from the early bud alfalfa and full-flower alfalfa stems averaged 22% and 18%,

respectively. The surface moisture contents were approximately the same at 5.5% (see Table 1), therefore indicating that the bio-oil–water content was due to either the sample's hydroxyl composition or the minor differences in process conditions. The respective water-insoluble fractions of the bio-oil were 30% and 35%, while the water-soluble fractions were 52% and 43%, respectively. (See Figure 4.) While the water-insoluble fraction constitutes the pyrolytic fractions derived from lignin, water-soluble fractions are the fractions that are produced from carbohydrates. The water-soluble fractions quantified by HPLC are presented in Table 4. Levoglucosan originates from the cellulose, while the acetic acid comes from the deacetylation of hemicellulose.<sup>18</sup> (See Figure 5.)

Ultimate analysis of the bio-oil and some physical characteristics are presented in Table 5. In comparison with the parent biomass, the carbon content of the pyrolysis liquids increased by some 14%, the hydrogen content increased by some 2%–3%, and a slight increase in nitrogen over the parent biomass (2%) was observed. The oxygen content decreased 7%–10% from the feedstock to pyrolysis liquids. The most significant change was the ash content: 0.3% in the pyrolysis liquids, compared to 8% in early bud alfalfa and 5% in the full-flower alfalfa feedstock. The mineral composition of the bio-oil also differed from that of the original feedstocks. The sulfur content was reduced by more than half and the chlorine content was reduced from a fraction percentage to the ppm level. Such changes would make the combustion of the alfalfa bio-oil a more environmentally friendly thermochemical process than direct combustion of the feedstocks. Importantly, the bio-oil produced is denser than water, which makes it easier to ship than the parent biomass. The combined reduction in ash and increased carbon and hydrogen content resulted in an increased HHV (by 33%–46%) relative to that for the original feedstocks. The calorific values of three replicates of bio-oil samples from the early bud feedstock (Figure 6) were in the range of 23314–28422 kJ/kg. Bio-oil from the full-flower alfalfa stems was in the range of 23732–28229 kJ/kg. The average values, on a dry basis, were 33138 and 32887 kJ/kg for the early bud and full flower feedstocks, respectively, compared to heavy fuel oil, which has a HHV of 41000 kJ/kg.

**3.4. Charcoal Coproduct.** As mentioned previously, 34%–39% charcoal was produced, along with the bio-oil, during the alfalfa stem pyrolysis. The proximate analysis of the charcoal (see Table 6) indicated a low fixed carbon content and low volatile matter content. Surprisingly, the ash content of the charcoal was very high, amounting to 50% of the charcoal from the early bud alfalfa and 45% for the full-flower stems. The high ash explains why the bio-oil had a very low ash content, because most of the minerals were concentrated in the char. Sulfur and chlorine were relatively more highly concentrated in the charcoal than in the biomass or in the liquids, which would make charcoal combustion less environmentally friendly, in terms of chlorinated or SO<sub>2</sub> pollutants. Both internal and external surface areas were extremely low (see Table 7). With a maximum of 1.8 m<sup>2</sup>/g multipoint BET surface area, the surface area was probably similar to that of the parent biomass which, although not measured, is usually on the order of 1 m<sup>2</sup>/g. This means that surfaces and interfacial pores were not able to develop under the pyrolysis conditions or because of the excessive ash content or both. With such low surface areas the charcoal accompanying the pyrolysis oil production has little potential use as an absorbent material unless it is further activated. Day et al.<sup>19</sup> found that charcoal from fast pyrolysis reactors has a low surface area, because of the short residence

**Table 3. Process Conditions for the Experimental Runs**

Maturity Stage	Early Bud			Full Flower		
	bud 1	bud 2	bud 3	flower 1	flower 2	flower 3
Run Date	4/23/2007	5/23/2007	8/28/2007	5/16/2007	5/31/2007	8/14/2007
Operational Conditions						
Biomass [g]	1994	1889.8	1456	1762	1869	1778
Feed Rate [g/h]	1407.53	952.84	1004.14	832.31	1038.33	1481.67
Bed Temperature [°C]	509.09	439.03	520.96	485.91	493.54	483.64
Condenser #1 Temperature [°C]	259.21	248.65	231.93	210.49	202.86	260.11
Condenser #3 Temperature [°C]	71.53	65.19	83.77	71.55	76.54	87.58
Condenser #4 Temperature [°C]	48.11	45.68	56.01	48.14	53.83	51.18
ESP Temperature [°C]	36.59	37.12	41.46	36.05	43.2	31.57
Heat Rate [°C/s]	4423	3826	4577.6	4256	4326	4235
Total Quench Rate [°C/s]	50.14	47.64	42.9	39.29	35.96	51.47

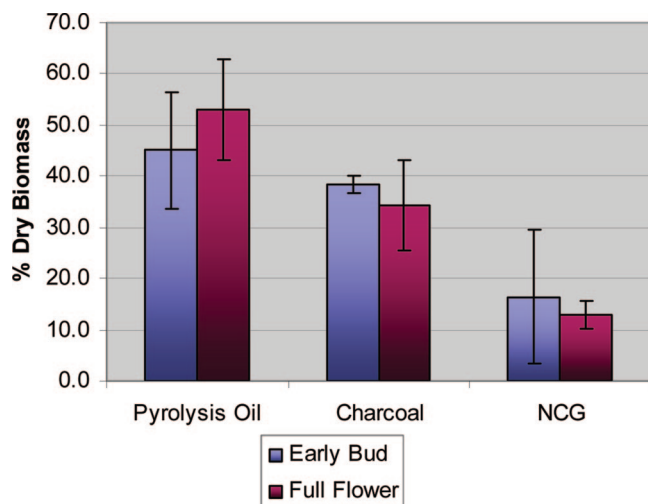
time in the reactor. In our case, the residence time in the reactor was only a fraction of a second.

**3.5. Noncondensable Gas (NCG).** As mentioned previously, the noncondensable gas (NCG) from the early bud and the full-flower feedstocks were 16.3% and 12.8%, respectively, of the pyrolysis products. This is relatively high, compared to that of switchgrass (11.3%).<sup>14</sup> The distribution, normalized over nitrogen, which was used as the fluidizing gas (Figure 7), indicated a higher concentration of CO<sub>2</sub> in NCG from the early bud than for the full-flower feedstock. The low concentration of CO<sub>2</sub> and

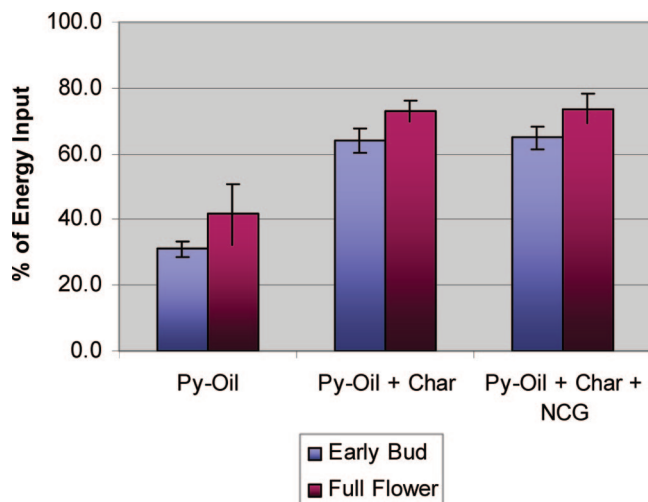
the high concentrations of CH<sub>4</sub> and H<sub>2</sub> make the cold NCG from the full-flower feedstock a better quality fuel gas.

#### 4. Discussion

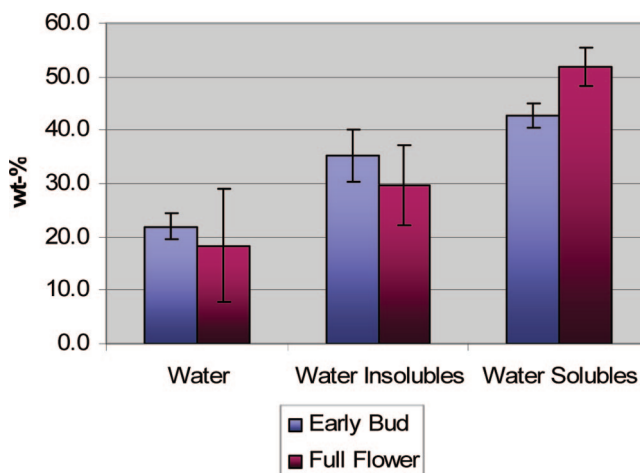
Biomass fast pyrolysis processes usually produce 60–75 wt % of liquid bio-oil;<sup>18</sup> however, lower average bio-oil yields were obtained in this study with alfalfa stems as the feedstock (45% early bud, 53% full flower). We have previously reported the fluidized-bed fast pyrolysis of switchgrass, which is another potential energy crop, with 60% bio-oil yield, using this same system.<sup>14</sup> The alfalfa stem bio-oil yield was apparently lost to higher char yields (>30%), although the NCG yields were also higher than obtained with switchgrass (11.3%). Higher char yields for alfalfa stems are at least partially related to the higher ash content of the alfalfa biomass (8.3 wt% for early bud, 5.5 wt% for full flower) versus switchgrass (2.5 wt %) and most woody biomass (<1 wt %) typically used in fast pyrolysis processes, because ash is concentrated in the char during the process. This result was reflected in the char yields of the two samples of alfalfa stems. Average char yield for early bud alfalfa



**Figure 2.** Product yields as percent of dry alfalfa stem mass; bars represent standard deviations. (NCG = noncondensable gas.)



**Figure 3.** Distribution of energy recovered from input biomass and reactor power supply; bars represent standard deviations.

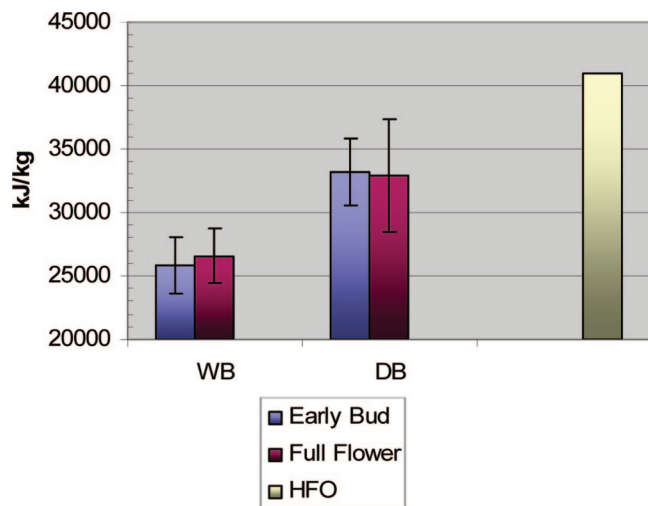


**Figure 4.** Entire oil fractions. Average of three runs is shown for each; bars represent standard deviations.

**Table 4. Water-Soluble Fractions of the Bio-oil Quantified (wt %)**

water-soluble component	Early Bud		Full Flower	
	water-soluble fraction <sup>a</sup> (wt %)	standard deviation (wt %)	water-soluble fraction <sup>a</sup> (wt %)	standard deviation (wt %)
levoglucosan	0.13	0.06	0.38	0.10
acetic acid	2.27	1.85	3.47	0.83
acetol	0.85	0.63	2.66	1.37
glyoxal	0.33	0.33	1.00	0.59

<sup>a</sup> Average of three oils produced.

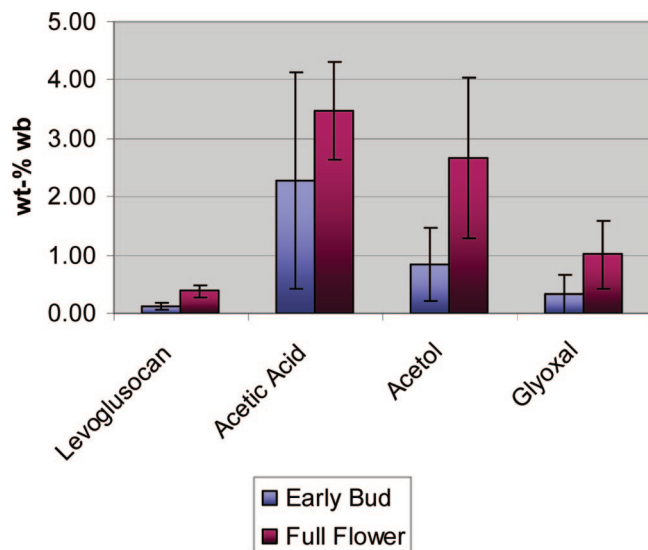


**Figure 5.** Soluble fraction components. Average of each for three runs (wb = wet basis); bars represent standard deviations.

**Table 5.** Bio-Oil Ultimate Analysis and Physical Characteristics<sup>a</sup>

	Early Bud	Full Flower
Composition		
carbon content (%)	53.755	56.995
hydrogen content (%)	8.45	7.885
nitrogen content (%)	4.575	3.745
chlorine content (ppm)	249.5	242
sulfur content (%)	0.053	0.0685
ash content (%)	0.2815	0.301
oxygen content, by difference (%)	32.66	31.295
Karl Fischer Water Content (%)	21.09	13.38
Heat of Combustion <sup>b</sup>		
(cal/g)	6178.8	6343.8
(kJ/kg)	25,852	26,542
Density (g/mL)	1.08285	1.14135

<sup>a</sup> Average of two unless otherwise noted. <sup>b</sup> Average of three.



**Figure 6.** Calorific value of the entire pyrolysis liquid product; bars represent standard deviations. (WB = wet basis; DB = dry basis; HFO = heavy fuel oil.)

stems was 38.5%, 34% for the lower ash containing full flower stems, and only 12.9% in the aforementioned switchgrass study. The decrease in ash and increase in cellulose and lignin content of the alfalfa stems associated with maturation from the early bud to full flower stages also explains the higher average bio-oil yield for the more mature feedstock. Additionally, the higher

**Table 6.** Charcoal Ultimate Analysis

	MW	Composition [wt %]		
		as received	dry basis	dry-ash-free (DAF) basis
Biomass at Early Bud				
Proximate Analysis				
Moisture		3.66		
Ash		50.63	52.55	
Volatile Matter		17.51	18.17	38.30
Fixed Carbon		28.21	29.28	61.78
Total		100.00	100.00	100.00
Heating Value				
[cal/g]		4572.00	4746.07	7506.04
[kJ/kg]		19129	19858	31405
Ultimate Analysis				
Moisture content	18	3.66		
Ash content		50.63	52.55	
H content	1	2.08	2.16	4.55
C content	12	39.73	41.23	86.88
N content	14	1.40	1.45	3.06
Cl content	35.5	0.97	1.01	2.12
S content	32	0.21	0.22	0.46
O content	16	1.34	1.39	2.93
total content		100.00	100.00	100.00
Biomass at Full Flower				
Proximate Analysis				
Moisture content		3.08		
Ash content		45.14	46.57	
Volatile Matter content		17.60	18.16	33.98
Fixed Carbon content		34.19	35.27	66.02
Total content		100.00	100.00	100.00
Heating Value				
[cal/g]		4982.00	5217.85	8617.42
[kJ/kg]		20845	21831	36055
Ultimate Analysis				
Moisture content	18	3.08		
Ash content		45.14	46.54	
H content	1	1.81	1.87	3.49
C content	12	37.06	38.28	71.54
N content	14	0.99	1.02	1.91
Cl content	35.5	0.74	0.76	1.43
S content	32	0.05	0.06	0.10
O content	16	11.15	11.47	21.53
total content		100.00	100.00	100.00

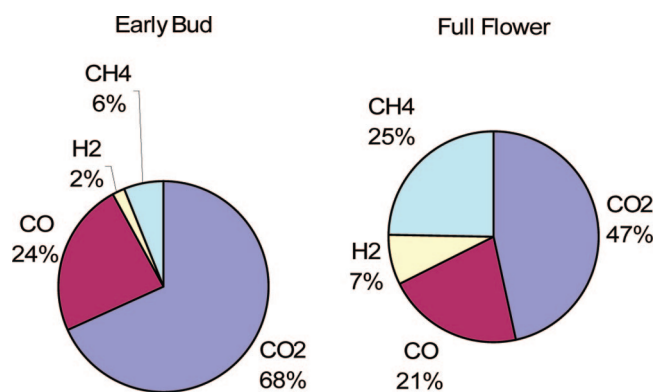
lignin content of the alfalfa stems over switchgrass forage could contribute to the lower bio-oil yield given that high lignin biomass such as bark is known to give lower (60%–65%) bio-oil yield;<sup>18</sup> however, this does not account for the high degree to which these alfalfa stem yields are lower. Other factors, including process conditions, could influence the shift from bio-oil to NCG. The high viscosity of the bio-oil requires one to maintain higher ESP temperatures in the condensers (to ensure flowability out of the ESP and prevent arcing), which leads to a lower quench rate. This could have resulted in secondary pyrolysis reactions further decomposing bio-oil components into NCG components or the inefficient condensation of some volatile bio-oil components, which adds those components to the NCG fraction.

Generally, the low yields of bio-oil produced from alfalfa stems is somewhat offset by the relatively high energy content of the bio-oil. Typically, bio-oil has an HHV of 16000–19000 kJ/kg,<sup>21</sup> which is 40%–50% of that of diesel fuel. The HHV of bio-oil in our previous study that was produced from switchgrass was in this range, at 18445 kJ/kg (as is). In the present case, the average heats of combustion were 25870 and 26561 kJ/kg for the bio-oils from early bud and full flower alfalfa stems, respectively; these values indicate an energy content of 65% that of diesel fuel, despite a moisture content of 20%. One factor that contributes to the high heats of combustion was the

**Table 7. Charcoal Surfaces and Interfaces**

parameter <sup>a</sup>	Average	Minimum	Maximum
Biomass at Early Bud			
Surface Area			
multipoint BET [m <sup>2</sup> /g]	1.006	0.572	1.274
single-point BET [m <sup>2</sup> /g]	0.848	0.460	1.060
BJH cumulative desorption surface area [m <sup>2</sup> /g]	0.495	0.319	0.639
DH cumulative desorption surface area [m <sup>2</sup> /g]	0.512	0.333	0.665
external surface area [m <sup>2</sup> /g]	0.115	0.041	0.166
micropore surface area [m <sup>2</sup> /g]	0.891	0.406	1.135
Pore Volume			
BJH cumulative desorption pore volume [cm <sup>3</sup> /g]	0.0065	0.0035	0.0080
DH cumulative desorption pore volume [cm <sup>3</sup> /g]	0.0062	0.0034	0.0077
micropore volume [cm <sup>3</sup> /g]	0.0004	0.0002	0.0005
Pore Size			
average pore diameter [Å]	266.63	255.30	283.50
BJH desorption pore diameter [Å]	38.33	33.99	42.93
DH desorption pore diameter [Å]	38.33	33.99	42.93
Biomass at Full Flower			
Surface Area			
multipoint BET [m <sup>2</sup> /g]	1.352	0.951	1.763
single-point BET [m <sup>2</sup> /g]	1.161	0.786	1.572
BJH cumulative desorption surface area [m <sup>2</sup> /g]	0.735	0.455	1.110
DH cumulative desorption surface area [m <sup>2</sup> /g]	0.749	0.467	1.125
external surface area [m <sup>2</sup> /g]	0.252	0.036	0.612
micropore surface area [m <sup>2</sup> /g]	1.099	0.915	1.233
Pore Volume			
BJH cumulative desorption pore volume [cm <sup>3</sup> /g]	0.0064	0.0041	0.0084
DH cumulative desorption pore volume [cm <sup>3</sup> /g]	0.0062	0.0040	0.0081
micropore volume [cm <sup>3</sup> /g]	0.0005	0.0004	0.0005
Pore Size			
average pore diameter [Å]	199.50	182.30	215.40
BJH desorption pore diameter [Å]	39.70	38.09	42.90
DH desorption pore diameter [Å]	39.70	38.09	42.90

<sup>a</sup> BET = Brunauer–Emmett–Teller method. BJH = Barrett–Joyner–Halenda method; D-H = Dolimore–Heal method.

**Figure 7.** NCG distribution, average over all runs.

relatively low oxygen and high carbon and hydrogen contents of the alfalfa stem bio-oils. Ultimate analysis of the alfalfa stems and the produced bio-oils reveal an unusual change in elemental composition from the parent biomass to bio-oil; the normally elemental composition remains constant from feedstock to bio-oil.<sup>18</sup> The oxygen content decreased by 6 wt % in the bio-oil for the early bud and by 9 wt % for the full flower alfalfa stems. Accompanying the decrease in oxygen content was an increase in carbon by 14 wt % and in hydrogen by 3 wt % for early bud alfalfa stems. The increases were 16 wt % and 2.5 wt % for

full flower alfalfa stems. The reasons for the change in elemental composition are unclear. The full flower alfalfa seemed to lose a large amount of oxygen to the char fraction; the char had an oxygen content of 11.15 wt %. However, this does not explain the similar loss of oxygen content for the early bud variety, as the char from this case averaged 1.34 wt% oxygen. Oxygen loss to NCG was more important for early bud alfalfa because of the higher NCG yield (16.3% vs 12.8% full flower) and its higher CO<sub>2</sub> content (68% vs 47% full flower, or 11% vs 6% from feedstock). The nitrogen content of the biomass (1.5%–2%) was concentrated in the bio-oil (3.2%–4.4%), which is a concern for producing NO<sub>x</sub> upon combustion. However, the bio-oils contained a reduced amount of other environmentally unfriendly elements, such as sulfur (~0.05 wt%) and chlorine (~250 ppm), versus the biomass feed (0.1–0.2 wt% S, 0.5 wt % Cl).

Analysis of the water-soluble fraction of the bio-oil revealed much lower than average levels of levoglucosan (<1 wt%), which is the major product of cellulose pyrolysis. There was slightly more levoglucosan in the bio-oils from the more mature feedstock, tracking with the cellulose content of the alfalfa stems feedstock. The low levels of levoglucosan in the bio-oil could be related to the high ash content of the feedstock, which is known to act as a catalyst to change pyrolysis decomposition pathways.<sup>22</sup> The low levoglucosan yield could also have been due to the process conditions, such as the low quench rate mentioned previously, leading to secondary pyrolysis reactions that could further breakdown levoglucosan into other products. Other water soluble compounds detected such as acetic acid, acetol and glyoxal, were all found at levels typical for bio-oils. (See Figure 5.)

Charcoal can be a valuable coproduct of bio-oil production. In fact, depending on the need for charcoal, pyrolysis can be optimized for charcoal production instead of bio-oil. Several applications have been proposed, including charcoal production as a carbon sequestration measure, soil amendment agent, and for nutrient delivery in a fertilizer system.<sup>19</sup> The heating rate used was >4000 °C/s (Table 3), which puts the current study in the fast pyrolysis mode that maximizes bio-oil production instead of char, which is maximized at a slower heating rate. Nonetheless, the charcoal produced is valuable for the applications mentioned if its properties are suitable for a specific application. For example, in soil amendment applications, high surface area (both internal and external), pore volume, and metal absorption affinity are some positive attributes for a charcoal coproduct.<sup>20</sup> However, char produced from fluidized bed fast pyrolysis generally does not have the high surface area that is required for such applications, and these cases were no exception (maximum surface area was 1.8 m<sup>2</sup>/g). Another application of charcoal is its use as combustion fuel to power an endothermic pyrolysis system, or it can be used independently as a solid fuel given that its energy content can be comparable to some coals.<sup>20,23</sup> Charcoal yields were >30% of the feedstock, with the early bud alfalfa stems having slightly higher charcoal yields than the full flower alfalfa stems. The heats of combustion of the charcoals were slightly higher for the more mature feedstock (19150 kJ/kg for early bud vs 20860 kJ/kg for full flower). However, the ash content of these chars was very high (~50%), an anomaly that can only be explained by the possibility of some sand from the reactor bed having leached into the char, artificially raising the ash content. When taken on a DAF basis, the HHVs of the charcoals increased to 31405 (early bud) and 36055 kJ/kg (full flower). These HHVs are similar or greater than those of low sulfur coals (29000 – 34000 kJ/kg, DAF),



with a sulfur content ( $<0.5\%$  DAF) the same or less than most low sulfur coals.

NCG, the other product, is also combustible and could provide some energy for a self-sustaining pyrolysis system. The alfalfa stems at the full flower stage of maturity produced NCG with a higher energy content, because of the higher percentage of the combustible gases hydrogen, carbon monoxide (CO), and methane (CH<sub>4</sub>) than the early bud alfalfa stems where the NCG contained a higher level of noncombustible carbon dioxide.

When all of these factors are taken together, more of the energy input (biomass and reactor heat) was recovered for the full flower alfalfa stems (74%) than for the less-mature early bud alfalfa stems (65%). Approximately 30%–40% of the energy content was recovered in both the bio-oil and charcoal fractions, and much less of the energy went to the NCG fraction.

## 5. Conclusions

Fluidized-bed fast pyrolysis of the full flower and early bud maturity stages of alfalfa stems was performed for bio-oil production. Bio-oil yields were lower (45%–53%) than that typically observed for the fluidized-bed fast pyrolysis of biomass. However, the bio-oils produced from alfalfa stems had higher calorific value than most bio-oils, with high heating values (HHVs) that were approximately two-thirds of that of crude oil, whereas bio-oil usually has an HHV that is approximately half that of crude oil. The maturity of the alfalfa stem feedstocks had small but important effects on the yields and energy content of the products. The more-mature full flower feedstock contained more cellulose and lignin and less ash than the less-mature feedstock. This led to slightly higher bio-oil yields at the full flower maturity stage. The energy content of the bio-oils was similar for the bio-oils from alfalfa stems of both stages of development. Overall, because of the higher bio-oil yield and slightly higher energy contents of the charcoal and noncondensable gas (NCG) coproducts, the overall energy recovery was higher for the more-mature alfalfa stems. This suggests that, although plant maturity had only a slight effect on bio-oil yield and energy content, when the energy in the coproducts is considered, the more-mature alfalfa stems may be a better choice for a pyrolysis (thermochemical conversion) feedstock, probably because of the increases in lignin that occur with alfalfa maturation.

## Acknowledgment

The authors wish to thank Rich Cook, Keith Henjum, Ted Jeo, Mike Mandel, Johnny Morphew, Kenneth Schaffer, Eric Tilman, Kenneth Todd, and Jhanel Wilson of ARS and Mark Schaffer of Advanced Fibers and Powders (AFP) for technical support. We would also like to thank Prof. Adeniyi Lawal and Dr. James Manganaro of Stevens Institute of Technology (Hoboken, NJ) for providing BET surface areas measurements.

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Received for review January 18, 2008

Revised manuscript received March 13, 2008

Accepted March 25, 2008

IE800096G